



Structural and Dielectric Properties of Bi₂O₃ Doped SrTiO₃ Ceramics

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Abstract: Bismuth oxide (10%) doped with 90% SrTiO₃ (ST) ceramic powders was synthesized by solid-state route technique. The effect of Bi⁺³ ions on the dielectric response of ST showed an increase in dielectric constant (ϵ_r) than undoped ST. Low dissipation factor ($\tan\delta$) for good dielectric applications. Bismuth doped ST contrary to the expectations exhibited the decreasing trend of permittivity from 303K-525K and afterwards showed increasing nature with relaxations. The microstructure was examined by field emission scanning electron microscope (FESEM). Some additional phases SrBi₃Ti₅O₁₈ and TiO₂ rutiles were detected by X-ray diffraction technique.

Keywords: Dielectric properties, Polarization, X-ray diffract meter, Ceramic titanates.

Introduction

SrTiO₃ (ST) is an ABO₃ perovskite material. The electrical properties of ST are greatly influenced by the dopant, method of preparation, sintering temperature and time. Recently in case of bismuth oxide doped ST a novel microstructure was observed which is useful in understanding the grain boundary barrier layer capacitors (GBBLC) and efficient ferro-electric relaxations have been observed for the industrial applications when Bi₂O₃ doped with Ba_{0.8}Sr_{0.2}TiO₃ ceramics [1]. Yu Zhi et al [2] reported the low temperature and high temperature dielectric properties. In this study the author is intended to make study of the structural, micro structural and dielectric properties of Bi₂O₃ doped ST Ceramics to decrease the sintering temperature of strontium titanate which have not been discussed in earlier literature.

Experimental Procedure

The ceramic samples of Bi₂O₃ 10% doped with 90% SrTiO₃ were prepared by solid state diffusion method. At the outset ST powders have been synthesized using the raw materials of SrCO₃ (99.9% purity) and TiO₂ (99.9% purity). The mixed powders were calcined at temperature 1400^oC for 13hrs and the shrinkage of compound was apparently identified. Latter ST was mixed separately with Bi₂O₃ and ball milled for nearly 12 hrs. After wards these samples were calcined at 1100^oC for 13hrs and the pellets of thickness 0.14cm and radius of 0.62cm have been prepared. The powders and the pellets sintered at 1200^oC for 4hrs were characterized using XRD (BRUKER X-Ray Powder Diffract Meter, CuK_α) at room temperature and HIOKI 3532-50 LCR HiTESTER (Japan) for structural, surface morphological analysis and dielectric properties respectively. LCR controller over the temperature range from RT to 600^oC operated at the frequencies from 42 Hz-5MHz having the heating rate of 0.5^oC/min used for dielectric properties.

Results and Discussions

Fig.1 shows the comparison diffractograms of pure and bismuth doped ST. The reflection planes were noticed in the spectra relating to the cubic perovskite structure. The effect of bismuth ions on the lattice parameter of undoped ST was clearly observed in this investigation. The presence of copper ions in pure ST decreases the lattice constant (a). The ‘a’ value was slightly increased to 0.3895nm. Because the ionic radius of Bi⁺³ (0.230nm) is more than that of Sr⁺² (0.144nm) [3]. As an inclusive of primary phases few second phases such as TiO₂ rutiles and Sr₂Bi₄Ti₅O₁₈ phases. The average crystalline size (D) using Scherer formula and average dislocation density (ρ) were established according to the following equations [4] and tabulated in Table.1.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1) \quad \& \quad \rho = D^{-2} \quad (2)$$

Where k is a constant and is equal to 0.9, θ is diffraction angle, λ=0.154056 nm (Cu_{Kα}) and β is full width half maxima. The huge increment in the intensity of diffraction lines depends on structure factor. At diffraction angle of 32.492° the maximum counts 16888 and similar miller indices (h k l) were noticed as (100), (110), (111), (200), (210), (211), (220) and (310) that of undoped ST. These were in agreement with standard JCPDS No. 35-734.

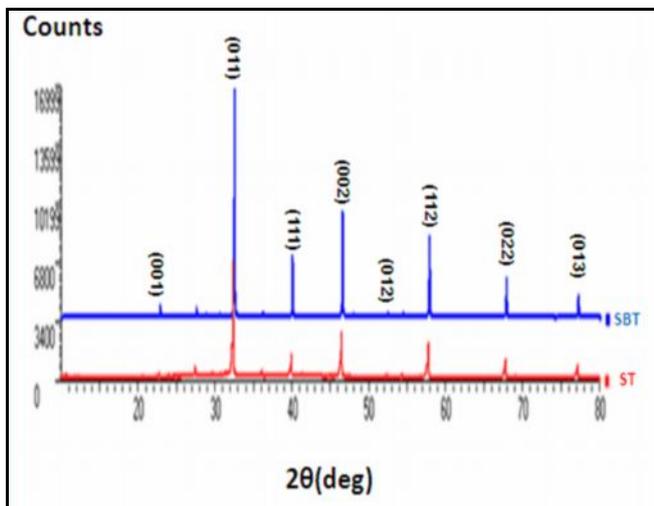


Fig.1 Shows the XRD Spectrum of pure and Bi₂O₃ doped SrTiO₃ ceramics

Table.1 Shows the XRD profile data of bismuth doped SrTiO₃ ceramics

| 2θ | d (Å) | D(nm) | ρx10 ⁻¹³ (m ⁻²) |
|--------|--------|-------|--|
| 22.842 | 3.8831 | 106.5 | 8.82 |
| 32.492 | 2.7178 | 117.5 | 8.81 |
| 40.049 | 2.2485 | 114.3 | 7.63 |
| 46.56 | 1.9482 | 106.0 | 8.9 |
| 52.439 | 1.7435 | 70.7 | 20.01 |
| 57.865 | 1.5918 | 97.3 | 10.56 |
| 67.908 | 1.3792 | 87.6 | 13.03 |
| 77.26 | 1.2339 | 79.0 | 16.02 |

Fig.2 shows the FE-SEM photograph made at 10,000 X magnification in 5µm range. Spherical shape grains including grain boundaries have been clearly observed. The average grain sizes (G_a) was calculated as 3.24µm using the linear intercept method []. The EDAX spectra showed the elements present in the compound with their concentrations (Fig.3). No other impurity elements were present except Sr, Ti, O and La elements. The wt% and at% are mentioned in the inset image.

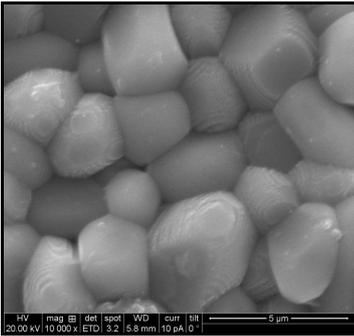


Fig.2. Shows the FESEM image of Bi₂O₃ doped SrTiO₃ ceramics

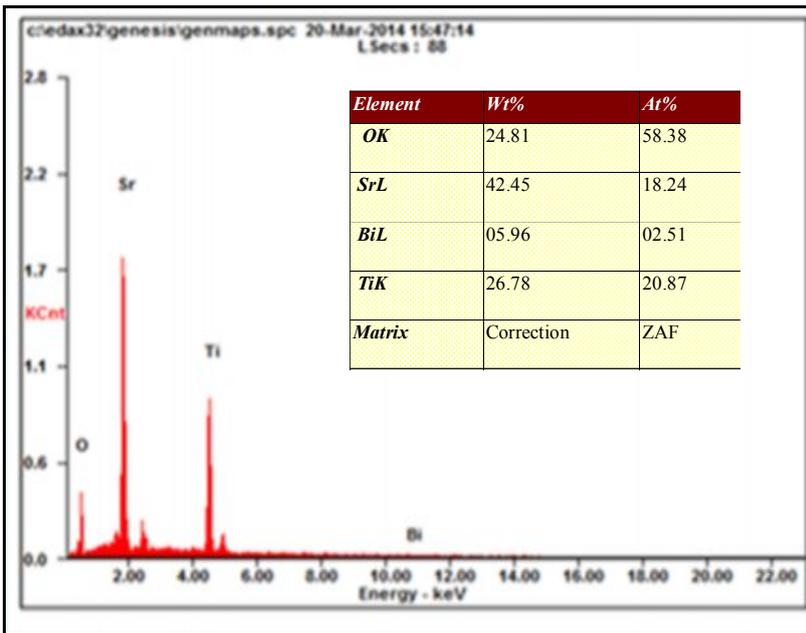


Fig.3. Shows the EDAX spectra of Bi₂O₃ doped SrTiO₃ ceramics

FTIR spectra of bismuth doped ST is depicted in Fig.4. It exhibited two broad bands at the wave numbers 690.4 cm⁻¹ and 766.5 cm⁻¹. These were corresponding to the presence of metal oxide (Ti-O, Sr-O and Bi-O) stretching vibrations.

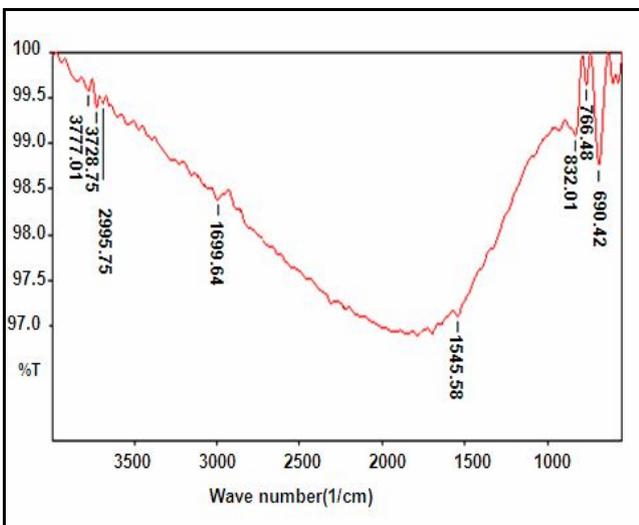


Fig.4. Shows the FTIR spectra of Bi₂O₃ doped SrTiO₃ ceramics

In case of bismuth doped ST permittivity (Fig.5) and loss (Fig.6) were decreasing with increase of frequency. These trends were approximately identical in case of undoped ST. At room temperature (RT) specimen exhibited dielectric constant (ϵ_r) of 214.6 at 10 kHz. A small improvement of permittivity is observed for bismuth doped strontium titanate (SBT) than pure ST. Very low loss factor ($\tan\delta$) of 0.00935 is reported in this study at RT. In respect of frequency variation of permittivity, high dielectric constant was obviously identified at low frequencies. But on going to the higher frequencies the permittivity is decreasing. Maxwell-Wagner interfacial polarization is responsible for this. Similar behavior is obtained in the literature [5, 6]. At low frequency while going to the high temperatures unsystematic trend of dielectric constant and loss were observed. This confirmed Low frequency of 0.1 kHz is not reliable. Low dissipation factor ($\tan\delta$) is suited for good low noise device applications. Bismuth doped ST contrary to the expectations exhibited the decreasing trend of permittivity from 303K-525K and afterwards showed increasing nature with relaxations. Apparently, bismuth doped ST was unable to induce permittivity but showed loss of at RT. Due to the high dielectric constant and low loss established at RT, bismuth doped ST performed the applications in electronic devices such as phase shifters, oscillators, micro wave tunable circuits, resonators and charge stored capacitors [5].

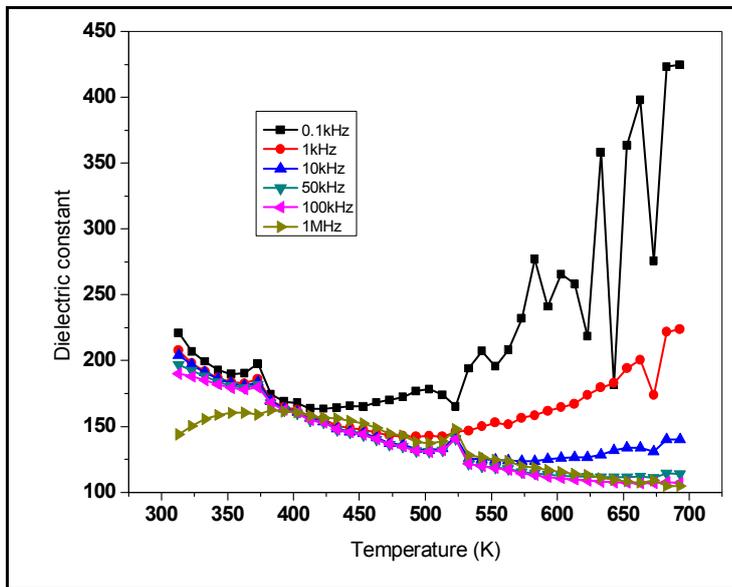


Fig.5. dielectric constant Vs temperature plots of Bi_2O_3 doped SrTiO_3 ceramics

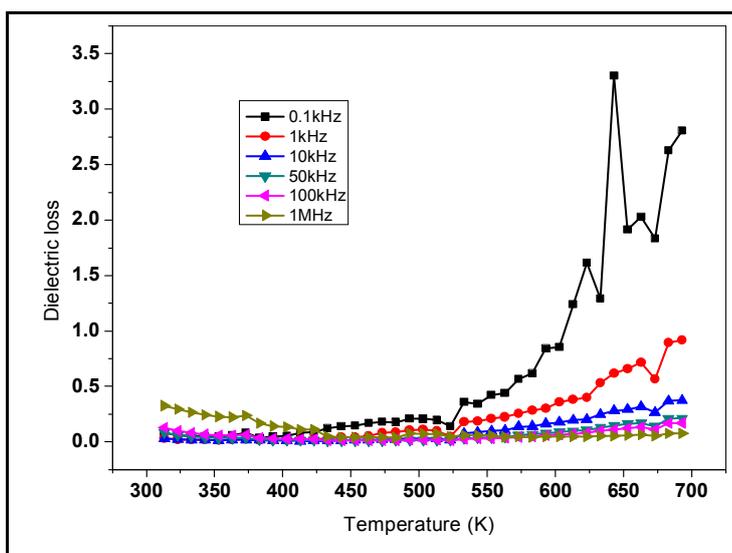


Fig.6. dielectric loss Vs temperature plots of Bi_2O_3 doped SrTiO_3 ceramics

Fig.7 showed the variation of ac-conductivity [7] with increase of frequency and temperature varying between 0.1 kHz-5 MHz and 30-430 °C. The plots expressed that conductivity is increasing with increase of

frequency and temperature. But interestingly, at 1 MHz frequency the decreasing trend of conductivity is observed. This may be due to the low hopping rate of charge carriers. Also, $\ln\sigma_{ac}$ versus $10^3/T$ plots were drawn and showed in Fig.8. The ac-activation energies are achieved as 0.24, 0.22, 0.15, 0.04, 0.01 and 0.12 eV according to the relation $\sigma_{ac} = \sigma_0 \exp(-E_a/K_bT)$, $K_b=8.6 \times 10^{-5}$ eV (Boltzmann constant). The decreasing trend of activation energy is due to increase of conductivity.

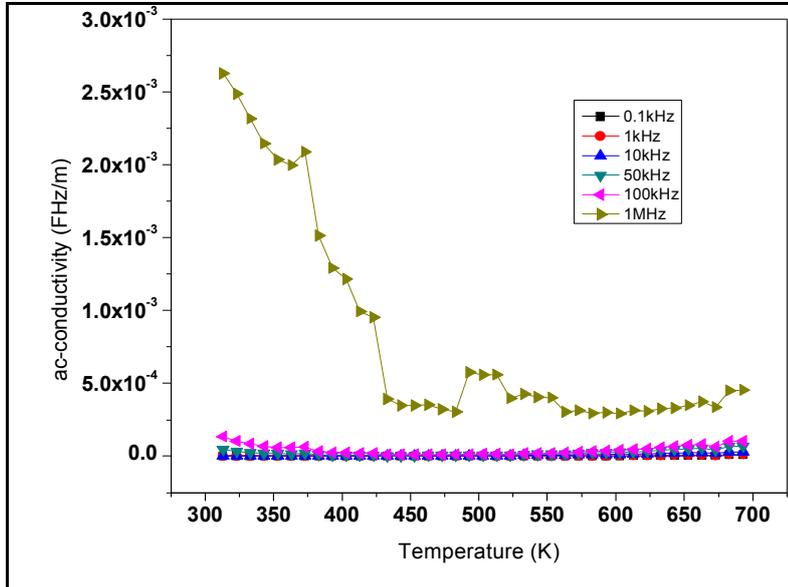


Fig.7. ac-conductivity Vs temperature plots of Bi_2O_3 doped SrTiO_3 ceramics

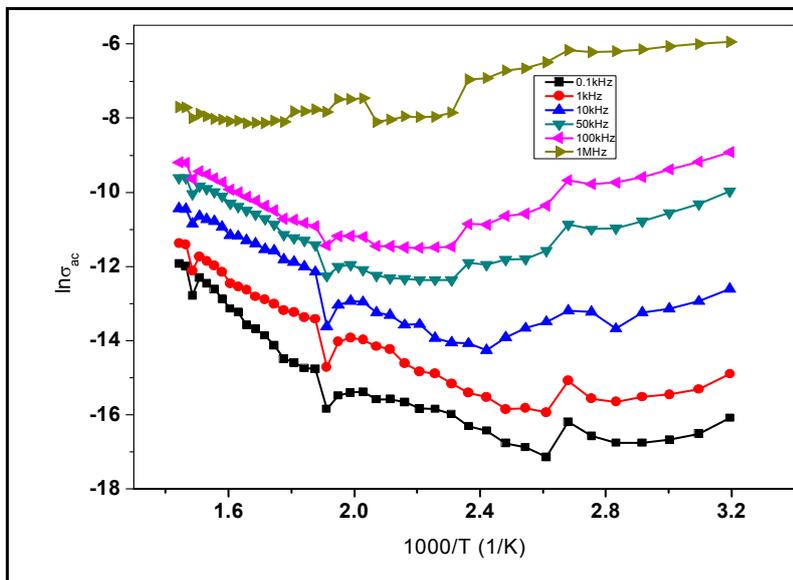


Fig.8. ac-conductivity Vs $10^3/T$ plots of Bi_2O_3 doped SrTiO_3 ceramics

Conclusions

Bismuth oxide (10%) doped with 90% SrTiO_3 (ST) ceramic powders was synthesized by solid-state route technique. Low dissipation factor ($\tan\delta$) for good dielectric applications. Bismuth doped ST contrary to the expectations exhibited the decreasing trend of permittivity from 303K-525K and afterwards showed increasing nature with relaxations. The microstructure was examined by field emission scanning electron microscope (FESEM). Some additional phases $\text{SrBi}_3\text{Ti}_5\text{O}_{18}$ and TiO_2 rutiles were detected by X-ray diffraction technique. At 1 MHz frequency the decreasing trend of conductivity is observed. The ac-activation energies are achieved as 0.24, 0.22, 0.15, 0.04, 0.01 and 0.12 eV.

Acknowledgements

This work was financially supported by a project of University Grants Commission (UGC)-NEW DELHI, INDIA. Also thanks to Vellore Institute of Technology (VIT), Tamilnadu, and Prof.K.R.Gunasekhar from IISC-Bangalore for supporting in characterization works such as XRD and SEM of my samples and giving their valuable suggestions.

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